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Passivation of Galvanized Surfaces to Improve their Corrosion Resistance

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Abstract

A systematic study has been performed to study the effect of concentration of Cr^{6+}, temperature of the bath and the temperature of galvanized products at the time of passivation, tolerance of the bath contamination and synergistic effects of some anions and cations with Cr^{6+} and Cr^{3+}, on the corrosion resistance performance of passivated galvanized surface. It is observed that the coating resistance increases with the concentration of the chromic acid (CA). The maximum salt spray resistance (about 100 hours) is observed at >=2% of CA. However, at this concentration, an objectionable yellow colouration appears at the surface. A rise in temperature of the bath results in an improvement of the resistance to white rusting. However, above 80°C, the performance is deteriorated. The temperature of galvanized surface has a deteriorating effect on the performance of the coating. Effect of some possible contaminants such as Na^{+}, Ni^{2+}, Cu^{2+}, SO_4^{2-} ,etc. have also been investigated. Electrochemical studies, surface reflectance, surface studies (SEM), EDAX etc have been performed to study its impact on the corrosion resistance of the coating.

INTRODUCTION :

Freshly galvanized surfaces are very prone to interact with the surroundings and form white powdery corrosion product which is generally hydroxide, carbonate or chlorides / sulphates. These powdery corrosion products are known as white rust. The protective properties of this white rust is extremely poor and the attack on the base metal i.e., Zinc is aggravated owing to the absorption of moisture and gases in this porous film. To avoid the formation of these powdery products on zinc surface, a protective film is applied to the surface which makes the surface resistant to the reduction of oxygen or water (in normal atmospheric corrosion these are the cathodic reactions). Literature survey has revealed thatchemical conversion coatings based on chromium compounds, tungstate and molybdate are applied to zinc surface to control the white rusting problems [1-5]. Out of these coatings provided on the surface of zinc, the coating based on chromium compounds is considered to be the most effective under the influence of variable parameters. This is owing to the fact that over a wide range of pH values, the Cr^{6+} ions are reduced easily to form protective chromic hydroxide film at a nobler potential than the corrosion potential of corroding zinc in an aqueous electrolyte. The mechanism of the action of this anion on the zinc surface to form protective layer is, however, not fully understood. Moreover, the influence of plant parameters and the correlation of the performance of the passivators based on chromium compounds with the electrochemical parameters; effect of cold forming and influence of some ions have also been scarcely attempted. These correlations are very important in view of the fact that they provide a quick result on the performance of passivators to be used in a system or in developmental programmes of passivators. In the present paper, an attempt has been made to address the above lacunae existing in the literature and suggest remedial measures.

EXPERIMENTAL DETAILS :

(a) Salt spray resistance tests : Salt spray resistance tests for the galvanized coatings were performed as per the specifications of B 117. Duplicate samples of size 5 cm x 7.5 cm were cut from the same sheet (original size of the sheet was 300 cm x 100 cm) produced in hot dip batch type of galvanizing. The sheets were collected from the plant in unpassivated state. To remove any trace of grease/oil or other impurities present on the specimen during its handling, they were degreased with MgO paste and then washed thoroughly. All the edges of the specimen were

covered with a good quality water resistant tape. The passivation treatment to the surface was provided by instantaneous dipping of the specimen in passivation bath and then taking them out through a structure having rubber lining. This completely wipped off the passivation solution from the surface of the specimen. It was observed that the contact time between the solution and the specimen was about 1-2 seconds. After giving the treatment to the specimen, they were hanged in laboratory atmosphere for 48 hours to stabilize the passivation film on the surface. After exposing the specimen in the salt spray chamber, observations were made after every 8 hours. Out of the two specimen, the specimen which lasted for maximum period of exposure against white rusting was taken as the right specimen and observations were recorded for that specimen only. This technique was adopted due to the reason that the white rusting could start due to some other defects already present on the galvanized coating.

To determine the role of corrugation on the performance of the coating, the specimen were passivated in the laboratory and corrugation was carried out in the plant. Different periods of stabilizing time to the film was allowed prior to corrugation. Some panels were cut from the corrugated sheets passivated and corrugated in the plants.

(b) Electrochemical studies : Electrochemical studies were performed by cutting the flag types of specimen of 1cm^2 area from the same sheets as used for the salt spray tests. The procedures for the preparation of the specimen were the same as described for the salt spray tests coupons. The potentials were measured against saturated calomel electrode. A potentiodyne analyser (M/S Petrolite Corporation, USA) was used to run potentiodynamic polarization studies.

EXPERIMENTAL RESULTS :

Variation in salt spray resistance (white rusting) against the concentration of chromic acid (CA) is shown in figure 1. These observations were noted by maintaining the temperature of the treatment bath at room temperature (R T = 30^{o}C), 60^{o} and 80^{o}C. Another set of exeperiments were also performed by keeping the specimen in oven at 90^{o}C for 10 minutes and then passivating them in the chromic acid baths. This was carried out to study the effect of sheet temperature at the time of treatment, on salt spray resistance. In general, it is observed that the salt spray

resistance increases with increase in concentration of CA solution. Above 0.5% of the concentration of CA, the surface appearance was having yellow tinge which is objectionable to sheet galvanizers. A 100 hours of salt spray resistance which is considered as the landmark for providing a considerable life of sheets against white rusting, is achieved only when the concentration of the bath is maitained >= 1.5% CA .

The plot showing the effect of temperature on salt spray resistance (S S R) for the specimens treated in 1% CA bath, indicates that the performance increases with rise in temperature (fig-2). The sheet which was having 90^{o}C temperature prior to passivation, has however, shown very poor performance.

Effect of the addition of some metal cations namely Na^{+}, Cu^{++}, and Ni^{++} as their sulphates on W.R. is shown in figure 3. An improvement in resistance against W.R. is observed in all the cases up to the concentration of 0.1% of cations. Above this concentration, a deterioration in W.R. resistance is noted in all the cases. The most pronounced effect is noted for Cu^{++}. It is to be noted here that although a deterioration has taken place at the higher concentrations of cations, the performance is still superior than in their absence except Cu^{++}, who exhibits the greater degree of deterioration at 0.5%, but has a W.R. resistance equivalent to in its absence i.e, 30 hours.

Na^{+} is not expected to have any influence on the passive film formation. An improvement in W.R. in the presence of Na_2SO_4 therefore, may be attributed to SO_4^{--}. This anion is indeed reported to have a positive role on the film formation 6. Copper and Nickel which are cathodic to zinc are expected to deteriorate the corrosion resistance of galvanized coating,howeverr, appear to have an improving effect due to the presence of SO_4^{--}.

Effect of some proprietary passivators : Two proprietary passivators designated as 'C ' and 'P ' were also evaluated to control W.R. in salt spray exposure and actual field exposure in marine environment of Digha (Bay of Bengal). These passivators were also evaluated for their performance to control W.R. on corrugated sheets. The results are summarized in Table I. It is evident from the Table that 'P ' provides optimum resistance to W.R. at the concentration of 2%, both in plain and corrugated sheets.

Table I : Performance of 'P ' and 'C ' passivators on W.R, surface reflectance and corrugation effect, bath temperature 50^{0}C, contact time, = 1-2 sec.

Parameters	Passivators and Concentrations					
	'P '			'C '*		
	1.0	2.0	3.0	1.0	2.0	3.0
1.Salt spray resistance(Plain Sheet)	48	>100	>100	30	48	100
2.Salt spray resistance(corrugated) within 1/2 hour of passivation	--	72	--	<24	--	--
3.Reflectance						
4.Surface Appearance	Bright	Bright	Bright	Bright	Yellow	Yellow

* 'C' above 1% produced yellow colouration

Table II : Effect of stabilizing time allowed for curing of passive film formed in presence of 2% of 'P'on galvanized surface, prior to corrugation, treatment time 1-2 seconds, squeezing of solution just after treatment.

Time allowed for curring (hours)	Salt spray* resistance to W.R.(hours)
0.5	72
2.0	66
6.0	48

*The specimen were putin salt spray chamber after 48 hoursof corrugation

The surface appearance was also quite brright in this case. Passivator 'C' however, provided only 30 and <24 hours of SSR at 1% of its concentration for plain and corrugated sheets, respectfully. Above this concentration an yellowish tinge appeared on the surface. Corrosion resistance of the film was also found to be deteriorated at the higher concentration. of 'C'. Very interesting observations were noted during the study of effect of curing time prior to corrugation on resistance to W.R

In case of 'C', a drastic reduction in S.S.R. was noted after corrugation. No effect of time of curing was observed in this case. In case of passivation by 'P', on the other hand, an improvement in S.S.R. was noted when the passivated surface was quickly (within 1/2 hour) corrugated (Table II). This was perhaps due to the reason that 'P' in its composition incorporates certain ingredients which retains passivating solution in invisible form, on galvanized surfaces, even after squeezing and drying. During corrugation, the additional compression energy supplied to the surfacce, helps in faster reaction of the passivator and it covers and passivates the broken film which may had been taken place due to the pressing effect of corrugation machine. This view is further corroborated with the microstructure of film formed in the presence of 'P' and 'C' (Figure - 4). It is observed that 'C' provides a lamellar type of structure on the zinc surface which is liable to be broken easily. In contrast to this, the film formed in the presence of 'P' is amorphous in nature and can withstand the cold deformation of the surface. Some photographs showing the effect of passivators on S.S.R. to W.R. are shown in figure - 5.

ELECTROCHEMICAL STUDIES :

Changes in open circuit potential (OCP) of galvanized sheets with passage of time in different concentrations of CA are shown in figures 6 . In very dilute solution of CA (0.1%), the potential initially jumps in more active direction. After 2 minutes of exposure, it gradually moves in nobler direction and stabilizes after 5 minutes. In 0.5%, the trend is reversed. The potential moves towards nobler direction and remains stable between 2-3 minutes. After this period of exposure, a continuous shift in active direction is observed. In concentrated solutions of CA i.e., 1% and 1.5%, the potential is stable initially for 3-4 minutes and then moves continuously in active direction.

Shifting of potential in active direction indicates either a cathodic polarization or an anodic depolarization, wheras an anodic shift indicates that the reaction is either anodically polarized or cathodically depolarized. During the film formation on zinc surface in the presence of hexavalent chromium solution, a cathodic depolarization reaction is always preferred. For an optimum film formation a treatment time of 1-2 minutes is sufficient. It is, therefore, this initial period of exposure (1-2 minutes) which is important in deciding the nature of passive film. In 0.1% CA, an initial shift of potential in active direction may be taken as the cathodic polarization (here reduction of Cr^{6+} to Cr^{3+}) as anodic depolarization is ruled out

due to very low amount of acidity present in the bath. After 2 minutes of exposure, an anodic polarization starts taking place. In this situation., the passive film formed on the surface is expected to be very weak resulting in poor protection. This is indeed observed during the salt spray test. In 0.5% CA, on the other hand, the potential immediately after exposure starts moving in nobler direction. This is a clear case of cathodic depolarization and following reactions take place :

$$Zn \text{ -------> } Zn^{2+} + 2e^{-} \quad \text{.....(i)}$$

$$Cr^{6+} + 3e^{-} \text{ ------> } Cr^{3+} \quad \text{.....(ii)}$$

A chromium chromate film is formed on the surface. This film is quite tenacious and protective and provides high degree of protection. A shift of potential in nobler direction may be attributed to the activation of reaction (ii).

In 1 and 1.5% of CA, an instantaneous thick film of chromium chromate is formed. Any further exposure of the specimen, a thickening in the passive film (potential shifting in active direction) takes place. This film provides an yellow colouration of the surface and does not have good corrosion resistance. This finding is also corroborated with the results as shown in figure - 6. The steady state corrosion potential of galvanized coating moves in nobler direction with increase in the strength of the acid, which is again an indication of facilitation of reaction (ii) which helps in the thickening of chromium chromate film formed on the surface, with time. Changes in OCP of the specimen treated in different concentrations of CA and exposed in 3.5% NaCl are shown in figures - 7 (A.D.). The specimen treated in 0.1% CA exhibits a continuous shift of OCP in active direction, indicating the formation of an inadequate thick film to stop the ionization of zinc from the surface (depolarization of anodic reaction). In case of 0.5% of CA treated specimen, however, the potential continuously moves in nobler direction (7-B) which indicates that the anodic polarization (zinc ionization) reaction dominates the corrosion process. The specimen having the treatment of 1% CA, exhibits an initial enobling of potential but after 4-5 minutes, a continuous shift of OCP takes place in active direction. This plot suggests that the film formed on the surface has an initial role in control of zinc ionization from the surface. However, with passage of time , a polarization of cathodic reaction (oxygen reduction) takes place. Passivation treatment using 1.5% of CA, exhibits a continuous enobling of potential which suggests that the passive treatment film is quite thick and during the period of exposure (10 minutes)

the film is sufficiently strong to withstand the ionization of zinc from the galvanized surface.

DISCUSSIONS :

Chromium compounds are considered to be one of the most effective passivating species towards the metals and alloys [7-8]. According to the widely held views, the passivation of metals by Cr^{6+} is due to their affecting the dissolution of metals through the formation of a complex oxide of dissolved metal (here zinc) and chromium. During the dissolution of zinc in acidic environments, dissolved oxygen is cathodically reduced at the interface of the corroding metal :

$$O_2 + 2H_2O + 4e^- = 4OH^- \quad .....(iii)$$

The chemisorption of these hydroxyl ions take place at the metal zinc surface :

$$Zn + 2OH^- = Zn(OH)_2 \text{ ads.} + 2e^- \quad .....(iv)$$

The reaction (iv) has a stimulating effect on zinc reaction with the acidic electrolyte of passivating bath (CA provides highly acidic environment) :

$$Zn(OH)_2 \text{ ads} + 2H^+ \text{-----} > Zn + 2H_2O \quad .....(v)$$

As is evident from equation (iv), the rate of reaction of formation of $Zn(OH)_2$ ads. at the corrosion potential region is controlled by the concentration of generated hydroxyl ions in the electrical double layer. This reaction is expected to be facilitated by the reduction of Cr^{6+} present in the solution :

$$2H_2CrO_4 \text{ (CA)} \text{-------} > HCr_2O_7^- + 2H^+ + OH^- \quad .....(vi)$$

$$HCr_2O_7^- + 3H_2 \text{ ------} > 2Cr(OH)_3 + OH^- \quad .....(vii)$$

$$Cr(OH)_3 + CrO_4^{--} + 2H^+ \text{ -----} > Cr(OH).CrO_4 + 2H_2O \quad ....(viii)$$

Chromium chromate protection film

The hydroxide formed at reaction (iv) and (vii) precipitates out the dissolved zincsimultaneously at the surface and provides the protective film to the galvanized surface. The above discussion clearly indicates that it is not simply the reaction products of zinc and Cr^{6+} compounds who decide the protective properties on to zinc surface but it is their mode of precipitation at the surface who decides the extent of protection. If above compounds are precipitated in such a fashion that an amorphous and adherent type of layer is formed at the surface, the passivator should provide a high degree of protection. This is indeed observed during the study of surface by SEM (fig - 4). An amorphous layer is produced in case of passivator 'P' which has provided very high degree of protection (Tables I & II)

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